

On the emission and the excitation spectra of SrS:Cu, CaS:Sm and CaS:Dy,Ce phosphors

Vijay Singh*, Manoj Tiwari¹ and S. J. Dhoble

⁰Department of Physics, Sadhu Vaswani College, Baragarh, Bhopal-462 030, Madhya Pradesh, India

¹Department of Physics, Bansal College of Engineering, Mandideep-462 046, Madhya Pradesh, India

²Department of Physics, Kamla Nehru College, Nagpur-440 009, Maharashtra, India

E-mail: vijayjiin@hotmail.com

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Abstract Green phosphors based on SrS and CaS have been developed for display applications. Sulphide based lamp phosphors activated with Cu, Sm, Dy and Ce were prepared by using solid-state diffusion method. Emission and excitation spectra of SrS:Cu, CaS:Sm and CaS:Dy,Ce phosphors were recorded at room temperature with the aim of their photoluminescence characterization. Their application as green emitting phosphors is discussed in this paper.

Keywords . Luminescence, doping, phosphors

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The SrS and CaS phosphors have the advantage that the electronic transitions concerned with their luminescence centers can be explained by simple monomolecular model, because their forbidden gaps are wider than those of ZnS phosphors. Sulphide based phosphors with impurity excited by Hg vapour line and its emission in the visible region of the spectrum is very useful in the lamp industries and in field of solid-state laser. Lumen output of sulphide phosphors does not decrease at high temperature for long time and its stability of chemical compositions is not disturbed. Metal sulphides in particular have found an important use as phosphors. Number of reports have appeared describing the spectroscopic properties of pure and activated sulphides and revealing applications of BaS, SrS and MgS in alloy semiconductors [1], radiation dosimetry [2] and fast high-resolution optically stimulated luminescence imaging [3]. Recently, ZnS phosphors have been prepared by Davies *et al* [4] for cathode ray tube, these phosphors have better potential luminescence properties as compared to standard commercial materials. Impurity-doped sulphide is interesting for a large number of base materials. It was, therefore, decided to conduct photoluminescence study of SrS and CaS

with Cu, Sm, Dy and Ce as activators for understanding the mechanism of luminescence and its application.

SrS and CaS based phosphors were obtained using solid-state reaction with control bearing between activators and CaSO₄ and SrSO₄ as starting material and fired at high temperature for 2 hours. AR grade carbon was used as a reducing agent during their synthesis. After heat treatment the melt was pulverized in a dry atmosphere and stored, keeping in view the extreme purity as the main consideration in preparation. A number of samples of CaS and SrS phosphors activated by Cu, Sm, Dy and Ce were prepared. X-ray diffraction technique was used to check the sample for proper crystallization. The details of phosphor preparation are the same as reported in earlier papers [5-7]. A measurement of PL spectra was recorded using FP-750 spectrofluorometer (Jasco, Japan) with red sensitive PM tube at room temperature.

SrS:Cu phosphor :

Figure 1 represents the photoluminescence spectra of SrS:Cu lamp phosphors. Figure 1 (curve-a) shows a broad band excitation peak 220 nm to 315 nm in the range of Hg emission spectra (emission wavelength is 484 nm). The overlapping of Hg

* Corresponding Author

emission spectra and excitation of SrS:Cu is the characteristic of lamp phosphors. The emission peak is observed at 484 nm (excitation wavelength is 274 nm) due to $3d^9 4s^1 \rightarrow 3d^{10}$ transition of Cu^+ ion in the green emission of spectrum. The incorporation of Cu ion in monovalent is the main part of synthesis of lamp phosphor. In the presence of carbon particles during synthesis of phosphor, it may be considered that Cu ion enters monovalent due to reducing atmosphere. Moharil and coworkers [8-10] have shown that Cu^+ emission depend on the types of procedures adopted during synthesis.

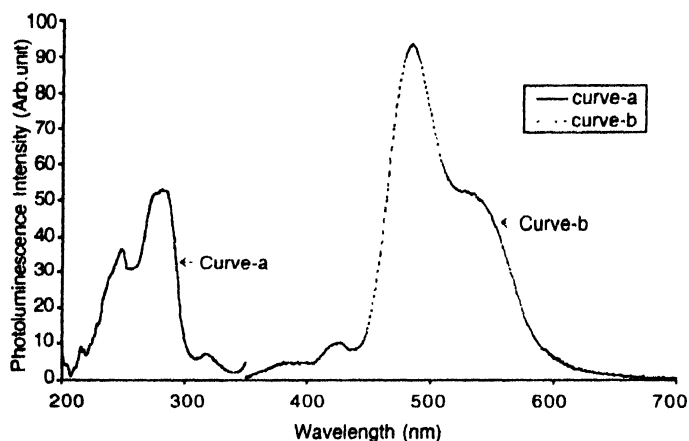


Figure 1. Photoluminescence spectra of SrS:Cu (0.05 mole%) Curve-a Excitation spectrum of SrS:Cu ($\lambda_{em} = 484$ nm) Curve-b Emission spectrum of SrS:Cu ($\lambda_{ex} = 274$ nm)

CaS:Sm phosphor :

Sm activator is used in lamp industry as red phosphor. It is difficult to observe sharp line in red emission of spectrum. CaS:Sm phosphor shows an excitation peak at 270 nm which is close to Hg excitation peak at 254 nm. In emission spectra of CaS:Sm excited by 270 nm (Figure 2 curve-b), multiple peaks are observed, strong emission is observed at around 573 nm and the other peaks are observed at 493 nm and 613 nm. The 493 nm peak due to Sm^{2+} ion and 573 and 613 nm PL emission peaks are due to $^4G_{5/2} - ^6H_{5/2}$ and $^4G_{5/2} - ^6H_{5/2}$ transitions respectively, of

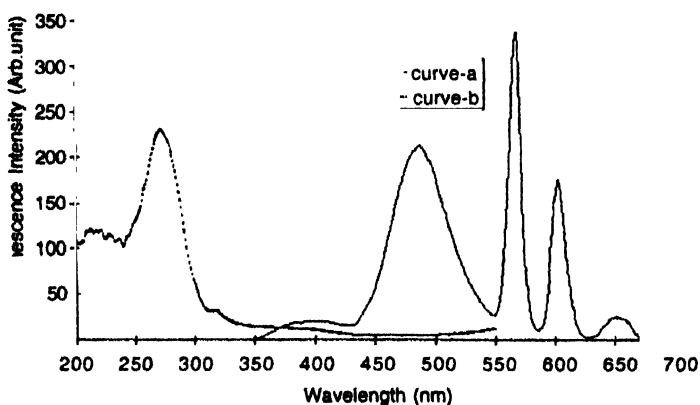


Figure 2. Photoluminescence spectra of CaS:Sm (0.1 mole%) Curve-a Excitation spectra of CaS:Sm ($\lambda_{em} = 573$ nm) Curve-b Emission spectra of CaS:Sm ($\lambda_{ex} = 270$ nm)

Sm^{3+} ions. This suggests that holes are trapped by Sm^{3+} ion within the vicinity of the Sm^{3+} sites and converted in Sm^{2+} ion. Hence in our prepared phosphor, Sm ion is observed in 2+ and 3+ state. On comparing photoluminescence of CaS:Sm phosphor with that of un-doped CaS phosphor, an emission peak is observed at 493 nm due to only Sm^{2+} ion in CaS:Sm phosphor. This peak does not appear in un-doped CaS phosphor. Thus we conclude that 493 nm peak is only due to Sm^{2+} ion. There are many workers [11-15] who believe that the Sm^{3+} ions in alkaline earth sulphides, act as electron traps and become Sm^{2+} after trapping electron. The first emission peak is at 493 nm, in green region and other two are in red region of the spectrum. Because of these characteristics of CaS:Sm phosphor, it may be used as green lamp phosphor as well as in tri-colour lamp.

CaS:Dy,Ce phosphor :

The excitation spectra of CaS:Dy,Ce (Figure 3 curve-a) show a strong peak at 272 nm. In the excitation peak, maximum part that overlapped the Hg emission peak was observed at 254 nm (Hg spectrum). When CaS:Dy,Ce is excited by 272 nm two peaks are observed, strong emission is observed at 523 nm and the other peak is observed at 446 nm and shoulder at 573 nm due to $^4f_{9/2} - ^6H_{13/2}$ transition of Dy^{3+} ion. A 446 nm peak shows pair formation of Ce-Dy ions in CaS lattice. The emission of Dy^{3+} is in the green range of spectrum. The proposed CaS:Dy,Ce compound may be used as a green emitting phosphor.

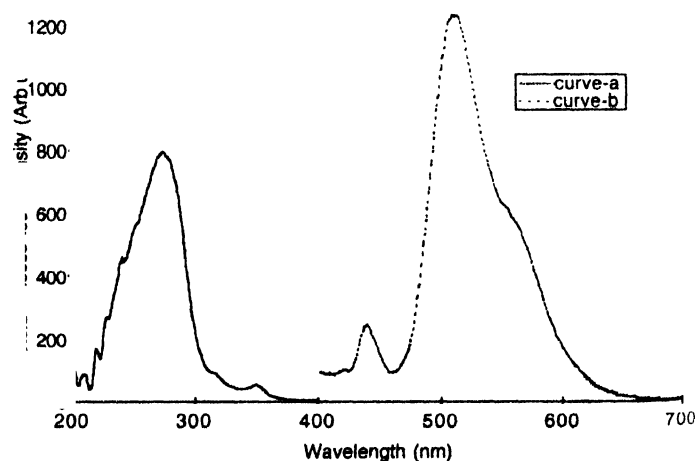


Figure 3. Photoluminescence spectra of CaS:Dy,Ce (0.1, 1.0 mole%) Curve-a Excitation spectra of CaS:Dy,Ce ($\lambda_{em} = 523$ nm) Curve-b Emission spectra of CaS:Dy,Ce ($\lambda_{ex} = 272$ nm)

Our experiments reveal that the excitation wave length of SrS:Cu and CaS:Dy,Ce phosphors lie within the range of 245 nm to 280 nm, which is within Hg vapor emission spectra and their emission spectra are very close to green region of spectrum. Therefore we propose that they may be used as green emitting phosphors. Three emission peaks of CaS:Sm phosphor are observed at 493 nm, 573 nm and 613 nm; while 493 nm peak is in the green region the other two peaks are in red region of the

spectrum. So it may be used as a tri-colour lamp phosphor. In this note we are not comparing our phosphors with the standard lamp phosphors. Our phosphors show prominent emission in green and red region of the spectrum. However, before these phosphors are used as lamp phosphors it must be ascertained that they fulfill the other requirements of a lamp phosphor. Work in this direction is in progress and will be reported shortly. The results are summarized in the Table 1.

Table 1. Spectral positions in the excitation and emission spectra of impurities doped sulphide phosphors

S. No.	Phosphors (mole %)	λ_{ex} (nm)	λ_{em} (nm)	λ_{em} (Intensity)
1	SrS:Cu (0.05)	274	484	93
2	CaS:Sm(0.1)	270	573	336
3	CaS:Dy(0.1),Ce(1)	272	523	1260

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